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(54) Title: ULTRA-HIGH-MOLECULAR-WEIGHT POLYETHYLENE PRODUCTS INCLUDING VASCULAR PROSTHESIS DEVICES AND METHODS RELATING THERETO AND EMPLOYING PSEUDO-GEL STATES

(57) Abstract

A pseudo-gel comprising a suitable solvent in an amount of 1 to 10 percent by weight and an ultra-high-molecular-weight polyethylene in an amount of 99 to 90 percent by weight, said polyethylene being a semicrystalline network with adjustable crystalline morphology comprising randomly dispersed and oriented chain-folded single crystals, stacks of single crystals, spherulite crystals, and extended-chain shish-kebab-type of fibrils with lengths up to a few millimeters and widths up to 20 μm. Also, the semicrystalline ultra-high molecular-weight polyethylene obtained by removal of said solvent from the pseudo-gel. Further, the method for making the pseudo-gel and the ultra-high-molecular-weight polyethylene product.

1     ULTRA-HIGH-MOLECULAR-WEIGHT POLYETHYLENE
2     PRODUCTS INCLUDING VASCULAR PROSTHESIS DEVICES AND
3     METHODS RELATING THERETO AND EMPLOYING PSEUDO-GEL STATES
4
5                S P E C I F I C A T I O N
6
7          This invention relates to a novel ultra-high-
8     molecular-weight polyethylene product, useful for vascular
9     prosthesis devices and for both industrial and biomedical
10    uses calling for high-impact, low-friction, high wear-
11    resistance, high-porosity, and softness or for one or more
12    of these qualities. The invention also relates to such
13    devices. It further relates to a novel method for processing
14    solution-grown ultra-high molecular weight polyethylene
15    crystalline morphologies which may form pseudo-gel states
16    when the polymer is dissolved in a suitable volatile or
17    non-volatile solvent at an elevated temperature and the
18    solution is cooled to or below the temperature at which the
19    polymer crystals are grown. Additionally it relates to
20    methods involving further processing of the pseudo-gel
21    states and their products after solvent extraction into
22    profiles and shapes with physical and mechanical properties
23    that may be tailored to specific biomedical (e.g., vascular
24    and orthopedic prosthesis and sutures) and industrial
25    applications.
26
27    Background of the Invention
28         Qualities such as softness, porosity, and bio-
29    compatibility have long been sought in the field of vascular
30    prosthesis.
31         The development of vascular prostheses has been a
32    subject of extensive work over the last 25 years. Most
33    synthetic vascular prostheses have been products of the
34    application of textile technology in this field and have
35    been woven or knitted tubular structures designed to
36    resemble the softness and flexibility of the natural blood
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1 vessels. The two major synthetic polymers used as vascular
2 prostheses have been Dacron polyester and polytetra-
3 fluoroethylene (PTFE).
4          These woven or knitted tubular structures are porous
5 and have been produced with smooth or velour surfaces. The
6 porosity, which has been claimed to play a determinant role
7 for the healing process of the arterial prostheses, can be
8 controlled to some extent by adjusting the thread size, or
9 the interstices size, and by the texturization or knit
10 pattern of the synthetic fabric. High degrees of porosity
11 may lead to excessive blood loss after implantation; the
12 velour has been claimed to have the advantage that it fills
13 the interstices of the underlying fabric, thus reducing
14 implant bleeding without reducing the porosity of the
15 implant.
16          The DeBakey Ultra-light-weight Knitted Prosthesis
17 (USCI, Inc.), the Cooley Graft and the Wesolowski Weavenit
18 (Meadox, Inc.) and the Microknit (Golaski Lab, Inc.) are
19 "smooth wall" commercial Dacron arterial prostheses of
20 different geometric and compositional configurations; the
21 Sauvage Filamentous Velour Prosthesis (USCI, Inc.) is an
22 example of a velour Dacron vascular prosthesis material.
23          Woven PTFE prostheses have low porosity and have not
24 been used as much as the Dacron prostheses. Also, it has
25 been suggested that their use should be temporary, their
26 permanent use being "dangerous". More recently, "expanded"
27 PTFE, called "Gore-tex" (W. L. Gore & Assoc., Inc.) has
28 become available. "Gore-tex" is a network of small nodules
29 interconnected by thin fibrils and with an adjustable
30 porosity from 0 to 96%, and it has been used with generally
31 encouraging results. Studies with smooth vascular prostheses
32 of expanded PTFE (85% porosity) and with ultra-light weight
33 woven PTFE showed that the patency (i.e., openness or non-
34 occlusion) of the expanded PTFE prostheses was significantly
35 longer (4.5 - 10 months) in comparison to the woven PTFE
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1 prostheses, which occluded in 101 days. It was also
2 demonstrated that the porosity played a critical role in the
3 healing process.
4        A recent theoretical calculation of the porosity in
5 woven fabrics shows that although their porosity can be
6 designed to vary over a wide range, the existing woven
7 vascular prostheses, e.g. Woven Cooley and Woven DeBakey
8 prostheses have had a low degree of porosity which might not
9 permit complete healing, particularly in small diameter,
10 low-blood-flow locations where the 5 year patency rate is
11 less than 30%.
12        Ultra-high-molecular-weight polyethylene (UHMWPE) is
13 another polymer which has attracted the interest of many
14 workers for the preparation of artificial prostheses,
15 particularly the construction of orthopedic joint devices,
16 because of its outstanding abrasion resistance and strength.
17 UHMWPE, in contrast to the conventional high-density poly-
18 ethylenes having average molecular weights up to approxi-
19 mately 400,000, has an extremely high molecular weight,
20 typically 2 - 8 million, and is intractable. The polymer is
21 supplied as fine powder and is processed into various
22 profiles using compression molding and ram extrusion
23 processes. The intractability of the polymer can be overcome
24 by varying the degree of material cohesion and its initial
25 morphology, more specifically by the formation of gel states
26 and single-crystal mat morphologies and by heating the
27 polymer melt to high temperature ranges, under inert
28 conditions, in which the viscosity of the melt is reduced
29 significantly for melt processing. The preparation of UHMWPE
30 gel states and single crystal mat morphologies have been
31 pursued predominantly for the development of ultra-high
32 modulus and strength fibers. Melt processing of UHMWPE at
33 high temperatures under inert conditions has been investi-
34 gated for the development of melt-crystallized morphologies
35 with enhanced mechanical properties which may result from
36 the material cohesion which is achieved by processing under
37 such conditions.
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1         Although the prior art covers to a large extent the
2 preparation of superstrong UHMWPE fibrous morphologies by
3 spinning processes which involve a gel intermediate, the
4 focus of the works has been mainly on the development of
5 filamentary products with high modulus and strength in one
6 direction. Also, there has been an expressed desire that
7 such filamentary products have reduced porosity, because
8 porosity may have an adverse effect on the effective
9 transmission of load within the oriented filamentary
10 products. On the contrary, the development of products with
11 bulk properties or enhanced isotropic mechanical properties
12 from gel-like precursors has received no attention.
13 Furthermore, little effort has been devoted to determining
14 the effect of the morphology of the gel-like precursor on
15 the physical properties and the deformability of the
16 products form gel-like precursors. These areas fall within
17 the scope of my invention and they have a potential impact
18 on the production of biomedical devices such as vascular and
19 orthopedic prostheses and sutures and also on the
20 fabrication of profiles possessing the outstanding wear
21 properties of UHMWPE.
22         An example of a stretched UHMWPE fiber and a process
23 for making it is U.S. Patent No. 4,413,110. There a slurry
24 of polymer in paraffin oil is heated to between $180^{\circ}$ and
25 $250^{\circ}C.$, preferably $200^{\circ}-240^{\circ}C.$ and is then cooled to a
26 temperature between $-40^{\circ}C$ and $+40^{\circ}C.$, the paraffin oil being
27 replaced by a more volatile solvent at a temperature below
28 $50^{\circ}C.$ and the cooling being rapid and done in such a way as
29 to produce a "gel fiber". This "gel fiber" is then treated
30 to evaporate the more volatile solvent and to stretch the
31 "xerogel" fiber, as it is called, at $120^{\circ}C + 160^{\circ}C.$,
32 preferably above $135^{\circ}C.$ The porosity of the resultant fiber
33 is stated to be "no more than about 10% (preferably no more
34 than about 6% and more preferably no more than about 3%)".
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## Summary of the Invention

The present invention includes the formation and use of UHMWPE pseudo-gels.

The term gel in the prior art referred to a macroscopically coherent structure, that (1) is spatially cross-linked, (2) comprises a major amount of low molecular-weight liquid, and (3) exhibits elastic properties not unlike those of solids.

On the contrary, in this specification and in the claims the terms "pseudo-gel" and "gel-like" refer to a concentrated solution of organic polymer which contains an entangled three-dimensional semicrystalline network the morphology of which may vary with the conditions of preparation or crystallization, for example, when the pseudo-gel of this invention is prepared under isothermal and quiescent conditions, the crystals in the pseudo-gel have predominantly a lamellar morphology, with single crystals on spherulitic crystals. The number of single crystals decreases, and the crystalline morphology becomes more complex as the solution concentration increases. On the other hand, when the pseudo-gel of this invention is prepared under non-isothermal and quiescent conditions, a large fraction of extended chain crystals (shish-kebab crystals) are also present. However, because the molecular entanglements in this semicrystalline network are not permanent, such solutions undergo flow when a shear stress, no matter how small, is applied. Therefore, such pseudo-gels exhibit time-dependent elastic properties and are not true gels, as the term is properly used, because they do not possess an equilibrium shear modulus.

In contrast to the prior art, the present invention provides for the preparation of an UHMWPE crystalline morphology with isotropic mechanical properties from a pseudo-gel precursor. Different crystalline morphologies are obtainable under different processing conditions. This crystalline morphology has an enhanced porosity which cannot

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1  be exhibited by melt-crystallized morphologies, and it is
2  readily deformable in the solid state into products with
3  different properties in one or more directions.
4       This invention provides a method for the preparation
5  of UHMWPE vascular prostheses by processing the UHMWPE in
6  the pseudo-gel state. The pseudo-gel is prepared by
7  dissolving a suitable concentration of the polymer in a
8  suitable solvent, preferably a non-volatile solvent, at an
9  elevated temperature well above the temperature at which the
10 pseudo-gel forms and then cooling to or below the
11 temperature at which the polymer crystals grow and the
12 pseudo-gel forms. The pseudo-gel is subsequently processed
13 under compression or tension into products of different
14 profiles. Extraction of the solvent from the shaped pseudo-
15 gel products leads to semi-crystalline porous morphologies
16 with geometrical configurations analogous to those of their
17 pseudo-gel precursors. These morphologies may be processed
18 further, at a temperature below or close to their melting
19 point.
20      This invention provides also a method for the
21 construction of vascular prostheses by (a) compressing the
22 pseudo-gels into thin films between hot plates, e.g., at
23 100-170°C., (b) wrapping the pseudo-gel film around a
24 rotating mandrel into a multilayer tubular structure, and
25 (c) extracting the non-volatile solvent from the tubular
26 structure on the mandrel, for example extracting first with
27 a more volatile solvent and then drying out the tubular
28 structure by evaporating the more volatile solvent.
29      This invention also provides for the preparation of
30 anisotropic UHMWPE morphologies with enhanced mechanical
31 properties, obtained by solid-state deforming, i.e., at a
32 temperature near or below the melting point of UHMWPE, the
33 semicrystalline polymer after extraction of the solvent, by
34 extrusion, drawing, molding, and forging techniques.
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1        This invention also provides for the preparation of
2 an UHMWPE semicrystalline material which has adjustable
3 porosity from zero up to more than 90%. This material can be
4 made with sufficient body to maintain its shape and cross-
5 sectional area; it is uniformly expansive and readily
6 deformable to generate products with bulk properties, in
7 contrast to filamentary products.
8
9 Brief Description of the Drawings
10
11        Fig. 1 is a flow sheet of a process embodying the
12 principles of the invention.
13
14        Fig. 2 is a flow sheet of another process embodying
15 the principles of the invention.
16
17        Fig. 3 is a flow sheet of a third process embodying
18 the principles of the invention.
19
20        Fig. 4 is an optical photomicrograph at about 100x
21 of a UHMWPE pseudo-gel morphology prepared under non-
22 isothermal and quiescent conditions (NIQ). The morphology
23 was viewed with cross-polarized light.
24
25        Fig. 5 is a reproduction of a scanning electron
26 micrograph of a UHMWPE semicrystalline morphology obtained
27 from the pseudo-gels after solvent extraction and drying,
28 according to the invention, the pseudo-gel having been
29 prepared under isothermal and non-quiescent conditions
30 (INQ).
31
32        Fig. 6 is a similar scanning electron micrograph
33 reproduction of a greater enlargement of the same kind of
34 UHMWPE semicrystalline morphology of this invention the
35 pseudo-gel having been prepared under isothermal and non-
36 quiescent conditions (INQ).
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1        Fig. 7 is an optical photomicrograph at about 100x
2 of a UHMWPE pseudo-gel morphology obtained under isothermal
3 and non-quiescent conditions (INQ). The morphology was
4 viewed with cross-polarized light.
5

6        Fig. 8 is a similar scanning electron micrograph
7 reproduction of a semicrystalline UHMWPE morphology of the
8 invention obtained from the pseudo-gel after solvent
9 extracting and drying, the pseudo-gel having been prepared
10 under isothermal   and quiescent conditions (IQ).
11

12        Fig. 9 is an optical photomicrograph at about 100x
13 of a UHMWPE pseudo-gel morphology obtained under isothermal
14 and quiescent conditions (IQ). The morphology was viewed
15 with cross-polarized light.
16

17        Fig. 10 is a graph plotting Young's modulus versus
18 draw ratio for a UHMWPE of this invention. The solid-line
19 curve represents observed values and the broken-line curve
20 shows estimated maximum values for the UHMWPE of this
21 invention.
22

23        Fig. 11 is a similar graph for a conventional
24 polyethylene, but not a UHMWPE.
25

26 Description of Some Preferred Embodiments of the Invention
27        As shown in Fig. 1, an UHMWPE pseudo-gel according
28 to this invention may be prepared from a raw UHMWPE powder
29 20 by dissolving the UHMWPE in a solvent at 21, preferably a
30 non-volatile solvent such as paraffin oil, in a temperature
31 range from 140 - 170°C., preferably in the high end of the
32 temperature range in order to disrupt the thermally
33 persistent extended chain morphology of the raw UHMWPE
34 powder and decrease the number of nucleation sites which
35 allow for the preparation, upon cooling, of large lamellar
36 single crystals. These are known to have a more regular
37 chain folded crystalline morphology than melt-crystallized
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1  and solution-grown crystal morphologies obtained by rapid
2  cooling, and therefore have fewer intercrystalline and
3  intracrystalline tie molecules. Such tie molecules affect
4  the deformation behavior of the semicrystalline morphologies
5  that are obtained after extraction of the solvent from the
6  pseudo-gel.
7          An UHMWPE used in this work was a HiFax 1900
8  (Hercules, Inc.) with an average molecular weight of 2 - 8 x
9  $10^6$. The UHMWPE was added slowly to the paraffin oil (MCB
10 Reagents, EM Science, PX 0045-3) to concentrations from 1 to
11 8% by weight. To avoid degradation of the polymer at high
12 temperatures, the polymer is preferably stabilized with
13 approximately 0.5 wt. % (based on the polymer) of BHT
14 antioxidant (butyl hydroxy toluene) and heated under inert
15 conditions.The mixtures were stirred slowly under constant
16 conditions at a temperature of 150°C. A solution 22 was
17 obtained that  appeared clear until it was cooled in step 23
18 to a temperature of approximately 123°C., where it became
19 opaque as the pseudo-gel was formed.
20         The uniformity of a so-produced UHMWPE pseudo-gel 24
21 depends on the conditions of preparation.  When the crystals
22 are grown in the concentrated solution under non-isothermal
23 and quiescent conditions, herein called NIQ, the UHMWPE
24 pseudo-gel is non-uniform and is comprised of a mixture of
25 single crystals and a fibrillar network in which the fibrils
26 have a shish-kebab crystalline morphology; the shish kebab
27 fibrils in the UHMWPE pseudo-gel can be up to 2 - 3 mm. long
28 and 20 μm. wide. This non-uniform structure is shown in Fig.
29 4.
30         The semicrystalline morphologies in Figs. 5 and 6
31 were obtained from the pseudo-gel shown in Fig. 7 which was
32 prepared under isothermal and non-quiescent conditions,
33 herein called INQ. These semicrystalline morphologies were
34 prepared by solvent extraction of the pseudo-gel followed by
35 drying. Fig. 5 is a scanning electron micrograph of such a
36 semicrystalline morphology; the degree of magnification is
37 shown by the white bar which corresponds to 0.1 mm. in the
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1 actual semicrystalline morphology. A further magnification
2 is shown in Fig. 6, when the white bar corresponds to 10 μm.
3 Fig. 7 is taken from an optical photomicrograph of the
4 pseudo-gel at about 100x and shows a typical shish-kebab
5 fibrillar structure surrounded by randomly oriented single
6 crystals and stacks of single crystals, as viewed with
7 cross-polarized light.

8         Thus, UHMWPE pseudo-gels prepared under either non-
9 isothermal or non-quiescent conditions exhibit remarkable
10 continuity and resistance to shear deformation.

11         The pseudo-gel shown in Fig. 9 was prepared under
12 isothermal and quiescent conditions, herein called IQ. When
13 the pseudo-gelation process occurs under isothermal and
14 quiescent conditions, the pseudo-gel is more uniform, has a
15 more turbid texture, and consists mainly of stacks of single
16 crystals and large spherulitic crystals (up to 200 μm in
17 diameter) with a significantly diminished fraction of shish
18 kebab fibrils, and resistance to shear deformation. Fig. 8
19 is a scanning electron micrograph of the semicrystalline
20 morphology obtained by solvent extraction and drying of a
21 pseudo-gel like that of Fig. 9.

22         The different crystalline morphologies of the UHMWPE
23 pseudo-gels obtained under different conditions of
24 preparation can be ascertained also by the thermal behavior
25 of the semicrystalline UHMWPE products which are obtained by
26 extracting, in step 25, the paraffin oil from the pseudo-gel
27 precursor with a more volatile solvent such as hexane, and
28 subsequently evaporating out, step 26, the volatile solvent
29 off in a drying process, leaving a semicrystalline UHMWPE
30 morphology 27. The results of the thermal analysis are
31 summarized in Table I.
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<u>TABLE I</u>

Thermal analysis data of semicrystalline
UHMWPE morphologies from gel-like precursors
of different concentrations and different
processing histories.

| Gel concentration (%W/W) | Tm (°C.) | Crystallinity (%) |
|---|---|---|
| 2 | 137 | 72 |
| 3 | 136.5 | 76 |
| 4 | 136.4 | 72 |
| 5 | 137 | 75 |
| 5* | 129.8 | 73 |

* Pseudo-gel preparation under isothermal and quiescent
conditions.

The first column of Table I indicates the percent
concentration of the gel-like precursor, the second column
the melting temperature of the semicrystalline morphologies
after the evaporation of the volatile solvent, and the third
column the percent crystallinity of these semicrystalline
morphologies. The melting endotherms were obtained at
5°C./min. under $N_2$, and the degree of crystallinity was
calculated, assuming that the heat of crystallization of a
perfect polyethylene crystal is 293 J/g.

The thermal analysis results indicate that the melting
temperature of the semicrystalline structures is independent
of the concentration of the gel-like precursors which were
obtained under non-isothermal non-quiescent conditions;
however, it is lower when the gel-like precursor was
prepared under isothermal and quiescent conditions. The
higher melting endotherm of the crystalline structures at
approximately 137°C. from pseudo-gels which were prepared

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1  under non-isothermal or non-quiescent conditions indicates
2  that the crystals should have an extended chain
3  configuration and is in agreement with the optical
4  observations (e.g., Fig. 4) that so-produced pseudo-gels are
5  comprised to a large extent of a shish kebab fibrillar
6  network.
7      The lower melting endotherm of the crystalline
8  structure at 129.9°C. from a gel-like precursor which was
9  prepared under isothermal and quiescent conditions (see
10 Figs. 8 and 9) indicates that the crystals in this case have
11 a chain-folded configuration, and, again, this is in
12 agreement with the observation that the isothermally
13 produced pseudo-gels under quiescent conditions are
14 comprised of chain-folded crystals, like the stacks of
15 single crystals and spherulites shown in Figs. 8 and 9.
16 Also, it is clear from the data in Table I that the percent
17 crystallinity of the semicrystalline structure is indepen-
18 dent of the studied concentration range of its gel-like
19 precursors as well as its processing history.
20     A semicrystalline UHMWPE structure which is prepared
21 from a pseudo-gel intermediate combines morphological
22 features which cannot be exhibited by the morphologies
23 obtained either by compacting the as-received fine powder
24 stock or by melt crystallization. These morphological
25 features arise from (a) the controlled material cohesion
26 which is incomplete in the compacted powders and the melt-
27 crystallized morphologies prepared by partial fusion,
28 (b) the diminished, _vis a vis_ the excessive, "amount of
29 physical entanglements" in the melt-crystallized morpholo-
30 gies prepared by complete melting, and (c) the great
31 variation of the crystalline morphology, from a chain-folded
32 to an extended chain crystalline morphology, depending on
33 the processing conditions during the preparation of the
34 pseudo-gel precursor. The importance of the first two
35 factors relates to the balanced enhancement of the deform-
36 ability of the semicrystalline structures from gel-like
37 precursors and their mechanical properties. The role of the
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1  third factor, and particularly the generation of a fibrillar
2  network, comprised of extended-chain shish-kebab crystals,
3  is important because such structure has a larger amount of
4  free volume and consequently a high degree of porosity.
5        In comparison to the knitted and woven textures whose
6  porosity can be adjusted to some extent by the thread size,
7  interstices size, and the texturization of the synthetic
8  fabric, the intrinsic fibrillar networks of this invention
9  have the advantage that their porosity can be adjusted by
10 thermal and mechanical means.
11       Thermal treatment may be brought about by heating the
12 semicrystalline structure from a gel-like precursor to a
13 temperature close to or above the melting point of the
14 polymer and then cooling to ambient under modest compression
15 ($\leq$ approximately 50 Atm). This treatment resulted in a
16 significant porosity reduction.
17       Similarly, when a semicrystalline structure from a
18 gel-like precursor was compressed at ambient temperature
19 under 500 Atm, its porosity was reduced as a result of the
20 densification process that takes place during the
21 compression process.
22       The porosity of the semicrystalline structure from a
23 gel-like precursor may be controlled also by the evapora-
24 tion rate of the volatile solvent during the drying process
25 as well as by solid-state deformation. The effects of
26 pressure, temperature, and solid-state deformation on the
27 percent porosity of UHMWPE semicrystalline morphologies from
28 gel-like precursors of different concentrations are
29 summarized in Table II.
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1                            TABLE II
2
3          The effect of temperature, pressure and solid
4          state deformation on the percent porosity of
5          UHMWPE semicrystalline morphologies from gel-
6          like  precursors of different concentrations.
7
8    UHMWPE Sample                                    Porosity (%)
9
10       NIQ - pseudo-gel, 1%                              90.5
11       NIQ - pseudo-gel, 2%                              51
12       NIQ - pseudo-gel, 4%                              63
13       SSD - pseudo-gel, 4%/DR = 4                       49
14       NIQ - pseudo-gel, 5%                              49
15       SSD - pseudo-gel, 5%/DR = 8                       40
16       INQ - pseudo-gel, 5%                              78
17       IQ  - pseudo-gel, 5%                              79.5
18       NIQ - pseudo-gel, 5%/compressed under 500 Atm     0.2
19       NIQ - pseudo-gel, 5%/heated to 140ºC./50 Atm      8.7
20       NIQ - pseudo-gel, 8%                              49
21    melt crystallized                                   7.3
22
23        NIQ = non-isothermal and quiescent conditions
24        INQ = isothermal and non-quiescent conditions
25        IQ  = isothermal and quiescent conditions.
26        SSD = solid state deformed
27        DR  = draw ratio
28
29     The     porosity     was     calculated     from    density
30  determination, assuming that the density of polyethylene is
31  960 kgm$^{-3}$. The symbol NIQ indicates that the gel-like
32  precursor was prepared under non-isothermal and quiescent
33  conditions; INQ indicates that the gel-like  precursor was
34  prepared under isothermal and non-quiescent conditions; and
35  IQ indicates that the gel-like  precursor was prepared under
36  isothermal and quiescent conditions.     SSD indicates a
37  semicrystalline morphology from an NIQ-pseudo-gel which was
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1 deformed in the solid state by tensile drawing at ambient
2 temperature and at the indicated Draw Ratio (DR) determined
3 by the cross-sectional areas before and after drawing.

4      The data in Table II indicates clearly that the
5 porosity of the semicrystalline UHMWPE morphologies from
6 gel-like precursors depends on the conditions of prepara-
7 tion and can be adjusted over a wide range from 0 to 90% by
8 a suitable choice of temperature and pressure, and solid-
9 state deformation.

10      As shown in Fig. 2, UHMWPE pseudo-gel states contain-
11 ing preferably a non-volatile solvent can be processed by
12 molding or rolling under compression in step 31 to obtain
13 thin gel-like film 32, preferably in a temperature range
14 close to or above the temperature at which the pseudo-gel is
15 formed (approximately 123°C.). Subsequently, the thin
16 pseudo-gel film 32 can be wrapped in step 33 with or without
17 tension on a mandrel to give a multilayer tubular structure,
18 a process which allows also for the build up of the tubular
19 wall thickness. Cohesion of the successive pseudo-gel layers
20 is achieved by a molecular reptation process which may occur
21 between adjacent layers and result in a tubular wall with
22 fraying resistance.

23      The volatile solvent such as n-hexane replaced the
24 non-volatile solvent in step 25 and is removed by evapora-
25 tion in step 34, to give a moderately shrunk, hoop stressed
26 structure 35,   in a drying step. Typically, the evaporation
27 of the volatile solvent from the pseudo-gel is accompanied
28 by considerable shrinkage, which when constrained has the
29 advantage of resulting in the development of hoop stresses
30 which enhance (a) the molecular chain orientation in the
31 circumferential direction and consequently the lateral
32 strength of the tubular structures and (b) the molecular
33 chain interpenetration in the overlapping pseudo-gel layers,
34 thus resulting in a coherent tubular wall.

35      Further enhancement of the mechanical performance of
36 the tubular structures can be achieved by solid-state
37 drawing in step 36 of the hoop-stressed dried tube 35.  The
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1 process may result in tubular products 37 having a biaxially
2 oriented fibrillar network structure with mechanical
3 integrity along and across the draw direction. This
4 integrity results from the superposition of the circumferen-
5 tial orientation, which is obtained by the constrained
6 shrinkage during the evaporation of the volatile solvent,
7 and the axial orientation during the solid-state deformation
8 process on the mandrel. The solid-state deformation was
9 performed at ambient temperature, and the draw ratio (DR)
10 was calculated from the displacement of markers on  the
11 tubular wall after drawing.
12      Fig. 10 shows in a solid line curve average experi-
13 mental modulus values at different draw ratios. The
14 variation of experimentally determined initial modulus with
15 the draw ratio is non-linear for the solid-state-drawn
16 UHMWPE semicrystalline morphologies of this invention to a
17 draw ratio of 8, in contrast to the previously established
18 linear relation for melt-crystallized, high-density (not
19 ultra-high molecular weight) polyethylene resins shown in
20 Fig. 11;  the difference is presumably due to the high
21 porosity of the UHMWPE semicrystalline morphologies, in
22 comparison to the low-porosity, melt-crystallized, high-
23 density polyethylenes, which diminishes and allows for
24 effective load transmission at significantly higher draw-
25 ratios. Fig. 10 shows in a broken-line curve a graph of
26 experimentally determined maximum initial modulus values
27 from my new material at different draw ratios.
28      Fig. 3 shows a process much like that of Fig. 2.
29 Pieces of pseudo-gel 40 are compressed at step 41 to make a
30 gel-like  sheet 42. The sheet 42 is wrapped around a mandrel
31 43 to produce a gel-like  tube 44, which is then extracted
32 at 45 to give a dry tube 46. This may be further processed,
33 as at 47, as by drawing, or may be received from the mandrel
34 43 to give a vascular product 48.
35      Alternative methods for the preparation of tubular
36 products with a biaxially oriented fibrillar network
37 structure include processes such as solid-state extrusion
38

1 through inverted conical dies and blowing air through the
2 tubes. Both processes are also suitable for the preparation
3 of biaxially oriented UHMWPE films which can be obtained by
4 splitting the biaxially oriented tubes along their length.
5 Also, some or most of the conventional thermoplastic
6 processes, such as rolling, extrusion, drawing, compression
7 molding, forging, and extrudo-rolling are amenable to
8 processing UHMWPE semicrystalline morphologies from gel-like
9 precursors into products with different profiles and
10 geometric configurations and with adjustable mechanical
11 properties over a wide range.
12      Tests _in_ _vivo_ indicate that artificial vascular
13 prostheses made by this process can be handled conveniently
14 and sutured to the natural vascular system readily. The
15 vascular prostheses, isotropic UHMWPE semicrystalline tubes
16 approximately 5 - 6 cm. long were implanted in the iliac
17 aorta of mature dogs for an observation period of up to four
18 months and exhibited very satisfactory anastomosis. Bleeding
19 through the wall of the prosthesis was not observed during
20 the implantation process. The prostheses are uniformly
21 expansive under the pulsatile blood pressure and are
22 flexible so that they bend without sharp corners. They do
23 not show aneurysms at and beyond the anastomatic interfaces
24 or along their body. (Aneurysms are local and progressive
25 enlargements of vessel because of loss of vascular
26 elasticity.)
27      The vascular prostheses of this invention can be
28 fabricated in different geometric configurations, straight,
29 crimped, smooth, or rough wall surfaces with adjustable
30 porosities and mechanical properties over a wide range.
31 Furthermore, this invention includes within its scope the
32 use of isotropic and anisotropic UHMWPE morphologies from
33 gel-like precursors in other biomedical application, such
34 as orthopedic prostheses, sutures, and ligatures, in which
35 a suitable combination of porosity and mechanical properties
36 is necessary.
37
38

1    Other polymers  which fall in the same category and
2 can be obtained from gel-like  precursors are ultra-high-
3 molecular-weight polypropylene, polyvinyl alcohol, and
4 nylons (polyamides).
5    To those skilled in the art to which this invention
6 relates, many changes in construction and widely differing
7 embodiments and applications of the invention will suggest
8 themselves without departing from the spirit and scope of
9 the invention.  Such embodiments may include the fabrication
10 of UHMWPE knitted and woven vascular prostheses, sutures,
11 and composite structures of UHMWPE filamentary and non-
12 filamentary semicrystalline morphologies. The disclosures
13 and the descriptions herein are purely illustrative and are
14 not intended to be in any sense limiting.
15    What is claimed is:
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- 19 -

1        1. A pseudo-gel comprising a suitable solvent in an
2    amount of 1 to 10 percent  by weight and an ultra-high-
3    molecular-weight polyethylene in an amount of 99 to 90
4    percent by weight, said polyethylene being a semicrystalline
5    network with adjustable crystalline morphology comprising
6    randomly  dispersed  and  oriented  chain-folded  single
7    crystals, stacks of single crystals, spherulite crystals,
8    and extended-chain shish-kebab-type of fibrils with lengths
9    up to a few millimeters and widths up to 20 µm.
10

11       2. The semicrystalline ultra-high molecular-weight
12   polyethylene obtained by removal of said solvent from the
13   pseudo-gel of claim 1.
14

15       3.  A  semicrystalline  morphology  of  ultra-high-
16   molecular-weight polyethylene comprising randomly dispersed
17   and oriented single crystals, stacks of single crystals,
18   spherulitic crystals,  and shish-kebab-type of fibrils with
19   lengths up to a few millimeters and widths up to 20 µm., a
20   melting point of 125 - 140°C., measured at a heating rate of
21   5°C./min., a crystallinity of about 70%, measured on the
22   basis that the heat of fusion of a perfect polyethylene
23   crystal is 293 J/g., and a porosity from about 50 to 90%,
24   measured on the basis that the density of polyethylene is
25   960 Kg/m$^3$.
26

27       4. A method for making an ultra-high-molecular-weight
28   polyethylene product for use in vascular prostheses and the
29   like, comprising,
30       dissolving ultra-high-molecular-weight polyethylene in
31   a solvent at an elevated temperature,
32       cooling the solution to  temperature at which polymer
33   crystals grow into an intercrystalline network that produces
34   a pseudo-gel state, and
35       extracting the solvent to produce a semi-crystalline
36   porous morphology.
37

38

1      5. The method of claim 4 wherein the cooling step is
2   done under non-isothermal, quiescent conditions.
3
4      6. The method of claim 5 followed by drawing the
5   semicrystalline morphology resulting from the extracting
6   step, at a draw ratio of at least 5 and at a temperature in
7   the range from ambient temperature to a temperature not
8   exceeding the melting point of said semicrystalline
9   morphology.
10
11      7. The method of claim 5, comprising, between the
12   cooling and extracting steps, the step of compressing the
13   gel.
14
15      8. The method of claim 4 wherein the cooling step is
16   done under isothermal, non-quiescent conditions.
17
18      9. The method of claim 4 wherein the cooling step is
19   done under isothermal, quiescent conditions.
20
21      10. A method for making an ultra-high-molecular-weight
22   polyethylene product for use in vascular prostheses and the
23   like, comprising,
24      dissolving ultra-high-molecular-weight polyethylene in
25   a non-volatile solvent at an elevated temperature,
26      cooling the solution to  temperature at which polymer
27   crystals grow into an intercrystalline network that produces
28   a pseudo-gel state, and
29      extracting the non-volatile solvent to produce a semi-
30   crystalline porous morphology.
31
32      11. The method of claim 10 wherein the cooling step is
33   done under non-isothermal, quiescent conditions.
34
35
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1     12. The method of claim 11 followed by drawing the
2  resulting product at a temperature no lower than ambient and
3  no higher than the melting point of the semicrystalline
4  porous morphology and at a draw ratio of at least 5.
5

6     13. The method of claim 11, comprising, between the
7  cooling and extracting steps, compressing the gel between
8  plates at 100° to 160°C.
9

10     14. The method of claim 10 wherein the cooling step is
11  done under isothermal, non-quiescent conditions.
12

13     15. The method of claim 10 wherein the cooling step is
14  done under isothermal, quiescent conditions.
15

16     16. A method for making a tubular profile of ultra-
17  high-molecular-weight polyethylene with adjustable wall
18  thickness, comprising the successive steps of
19     wrapping an ultra-high-molecular-weight polyethylene
20  pseudo-gel containing nonvolatile solvent on a mandrel,
21     extracting the solvent from the pseudo-gel with a more
22  volatile solvent, and
23     evaporating the volatile solvent from the tubular
24  profile.
25

26     17. The method of claim 16, comprising making an
27  anisotropic ultra-high-molecular-weight polyethylene tubular
28  structure by following the evaporating steps with the step
29  of stretching the tube on the mandrel.
30

31     18. The method of claim 17 in which the temperature of
32  stretching is from ambient temperature to the melting point
33  of the semi-crystalline porous morphology obtained after the
34  evaporating step.
35

36     19. The method of claim 17 in which the draw ratio is
37  at least 5x.
38

1        20. A method for making a tubular profile of ultra-
2  high-molecular-weight polyethylene with adjustable wall
3  thickness, comprising the steps of:
4        dissolving said ultra-high-molecular-weight poly-
5  ethylene in non-volatile solvent at an elevated temperature,
6        cooling the solution to  temperature at which polymer
7  crystals grow into an intercrystalline network that provides
8   a pseudo-gel,
9        wrapping the gel around a mandrel,
10        extracting the non-volatile solvent from the gel with
11  a volatile solvent, and
12        evaporating the volatile solvent from the tubular
13  profile.
14

15        21. The method of claim 20 followed by stretching the
16  tube on the mandrel at a temperature from ambient to 135°C.
17  and at a draw ratio of at least 5x.
18

19        22. A tube of ultra-high-molecular-weight polyethylene
20  semicrystalline morphology useful for vascular prostheses
21  and having a Young's modulus of at least 3 GPa obtained by
22  wrapping an ultra-high-molecular-weight polyethylene pseudo-
23  gel on a mandrel, extracting the solvent with more volatile
24  solvent and evaporating volatile solvent.
25

26        23. The tube of claim 22 in which the porosity is
27  adjustable over the range of 0.2% to 90%.
28

29        24. A pseudo-gel comprising a suitable solvent in an
30  amount of 1 to 10 percent  by weight and an ultra-high-
31  molecular-weight polymer in an amount of 99 to 90 percent by
32  weight, said polymer being a semicrystalline network with
33  adjustable  crystalline  morphology  comprising  randomly
34  dispersed and oriented chain-folded single crystals, stacks
35  of single crystals, spherulite crystals, and extended-chain
36  shish-kebab-type of fibrils with lengths up to a few
37  millimeters and widths up to 20 μm.
38

1    25. The semicrystalline ultra-high molecular-weight
2  polymer obtained by removal of said solvent from the pseudo-
3  gel of claim 24.
4

5    26. A semicrystalline morphology of ultra-high-
6  molecular-weight polymer comprising randomly dispersed and
7  oriented single crystals, stacks of single crystals,
8  spherulitic crystals, and shish-kebab-type of fibrils with
9  lengths up to a few millimeters and widths up to 20 μm., a
10 melting point of 125 - 140°C., measured at a heating rate of
11 5°C./min., a crystallinity of about 70%, and a porosity
12 from about 50 to 90%.
13

14    27. A method for making an ultra-high-molecular-weight
15 polymer product for use in vascular prostheses and the like,
16 comprising,
17     dissolving ultra-high-molecular-weight polymer in a
18 solvent at an elevated temperature,
19     cooling the solution to  temperature at which polymer
20 crystals grow into an intercrystalline network that produces
21 a pseudo-gel state, and
22     extracting the solvent to produce a semi-crystalline
23 porous morphology.
24

25     28. The method of claim 27 wherein the cooling step is
26 done under non-isothermal, quiescent conditions.
27

28     29. The method of claim 28 followed by drawing the
29 semicrystalline morphology resulting from the extracting
30 step, at a draw ratio of at least 5 and at a temperature in
31 the range from ambient temperature to a temperature not
32 exceeding the melting point of said semicrystalline
33 morphology.
34

35     30. The method of claim 28, comprising, between the
36 cooling and extracting steps, the step of compressing the
37 gel.
38

1     31. The method of claim 27 wherein the cooling step is

2 done under isothermal, non-quiescent conditions.

3

4     32. The method of claim 27 wherein the cooling step is

5 done under isothermal, quiescent conditions.

6

7     33. A method for making a tubular profile of ultra-

8 high-molecular-weight polymer with adjustable wall

9 thickness, comprising the successive steps of

10     wrapping an ultra-high-molecular-weight polymer

11 pseudo-gel containing nonvolatile solvent on a mandrel,

12     extracting the solvent from the pseudo-gel with a more

13 volatile solvent, and

14     evaporating the volatile solvent from the tubular

15 profile.

16

17     34. The method of claim 33, comprising making an

18 anisotropic ultra-high-molecular-weight polyethylene tubular

19 structure by following the evaporating steps with the step

20 of stretching the tube on the mandrel.

21

22     35. The method of claim 34 in which the temperature of

23 stretching is from ambient temperature to the melting point

24 of the semi-crystalline porous morphology obtained after the

25 evaporating step.

26

27     36. The method of claim 34 in which the draw ratio is

28 at least 5x.

29

30     37. A method for making a tubular profile of ultra-

31 high-molecular-weight polyethylene with adjustable wall

32 thickness, comprising the steps of:

33     dissolving said ultra-high-molecular-weight poly-

34 ethylene in non-volatile solvent at an elevated temperature,

35     cooling the solution to temperature at which polymer

36 crystals grow into an intercrystalline network that provides

37  a pseudo-gel,

38

- 25 -

1      wrapping the gel around a mandrel,

2      extracting the non-volatile solvent from the gel with

3  a volatile solvent, and

4      evaporating the volatile solvent from the tubular

5  profile.

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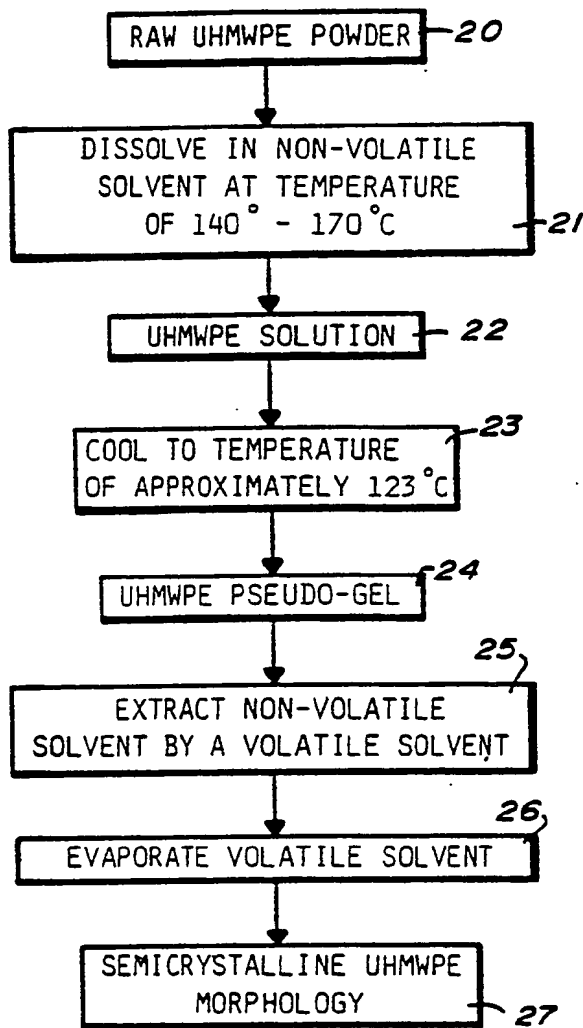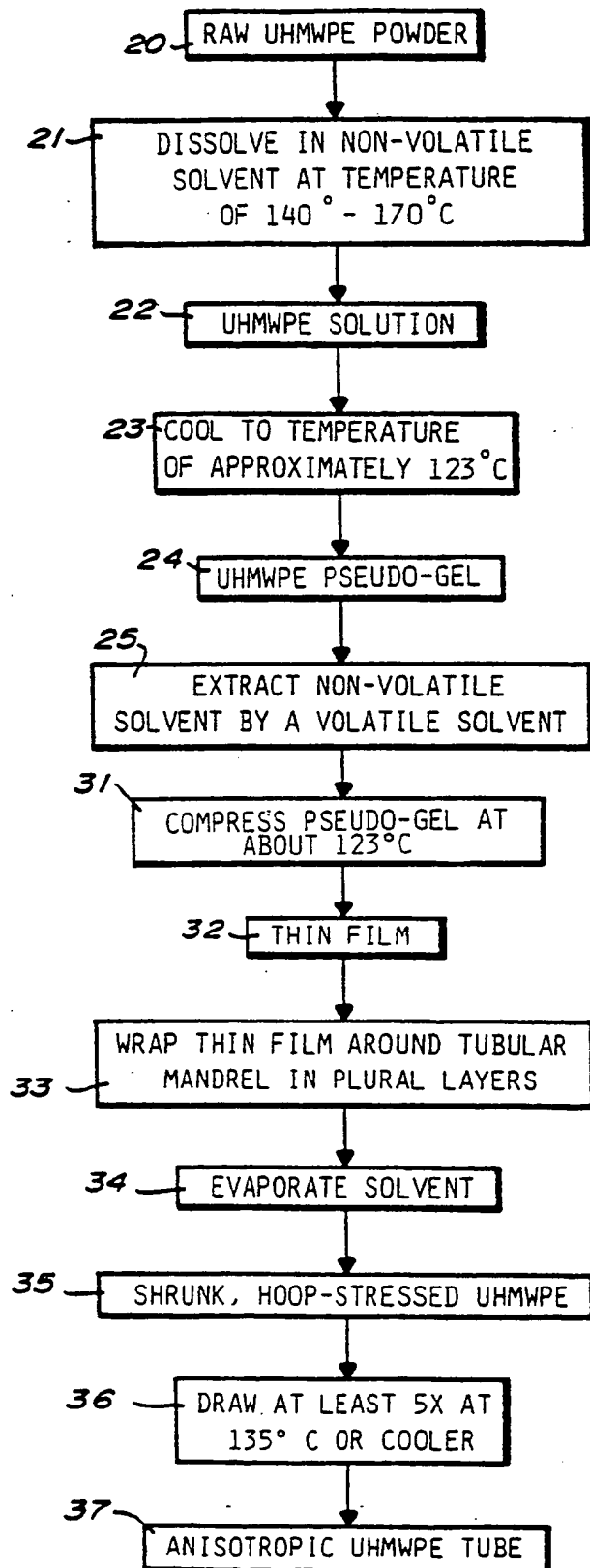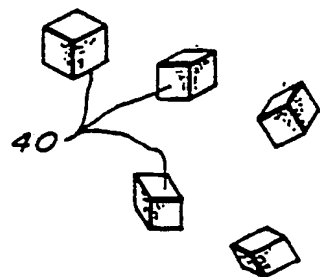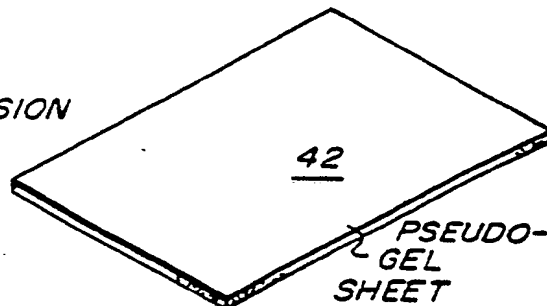
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FIG. 1

RAW UHMWPE POWDER —20

↓

DISSOLVE IN NON-VOLATILE
SOLVENT AT TEMPERATURE
OF 140° – 170°C —21

↓

UHMWPE SOLUTION — 22

↓

COOL TO TEMPERATURE
OF APPROXIMATELY 123°C —23

↓

UHMWPE PSEUDO-GEL —24

↓

EXTRACT NON-VOLATILE
SOLVENT BY A VOLATILE SOLVENT —25

↓

EVAPORATE VOLATILE SOLVENT —26

↓

SEMICRYSTALLINE UHMWPE
MORPHOLOGY —27

FIG. 2

20— RAW UHMWPE POWDER

↓

21— DISSOLVE IN NON-VOLATILE
SOLVENT AT TEMPERATURE
OF 140° – 170°C

↓

22— UHMWPE SOLUTION

↓

23— COOL TO TEMPERATURE
OF APPROXIMATELY 123°C

↓

24— UHMWPE PSEUDO-GEL

↓

25— EXTRACT NON-VOLATILE
SOLVENT BY A VOLATILE SOLVENT

↓

31— COMPRESS PSEUDO-GEL AT
ABOUT 123°C

↓

32— THIN FILM

↓

33— WRAP THIN FILM AROUND TUBULAR
MANDREL IN PLURAL LAYERS

↓

34— EVAPORATE SOLVENT

↓

35— SHRUNK, HOOP-STRESSED UHMWPE

↓

36— DRAW AT LEAST 5X AT
135° C OR COOLER

↓

37— ANISOTROPIC UHMWPE TUBE

# FIG. 3

PSEUDO-
GEL (IN PIECES)

40

COMPRESSION
41

42

PSEUDO-
GEL
SHEET

44

43 — WRAPPING WITH OR
WITHOUT TENSION

PSEUDO-
GEL TUBE

— MANDREL
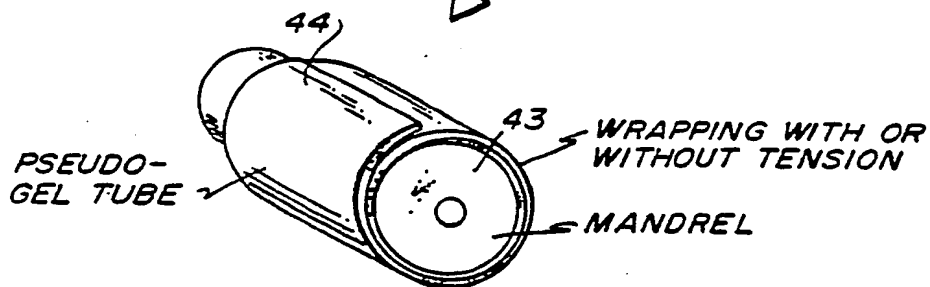
EXTRACTION
OF SOLVENT
45

DRY TUBE

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FURTHER
PROCESSING

REMOVAL
FROM MANDREL

48

— VASCULAR
PRODUCT
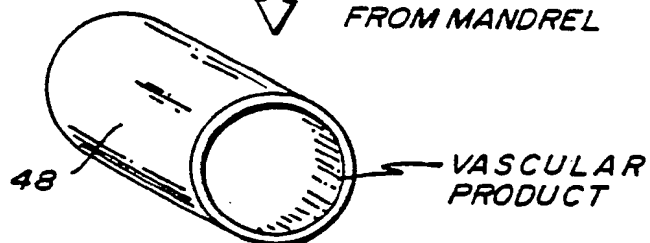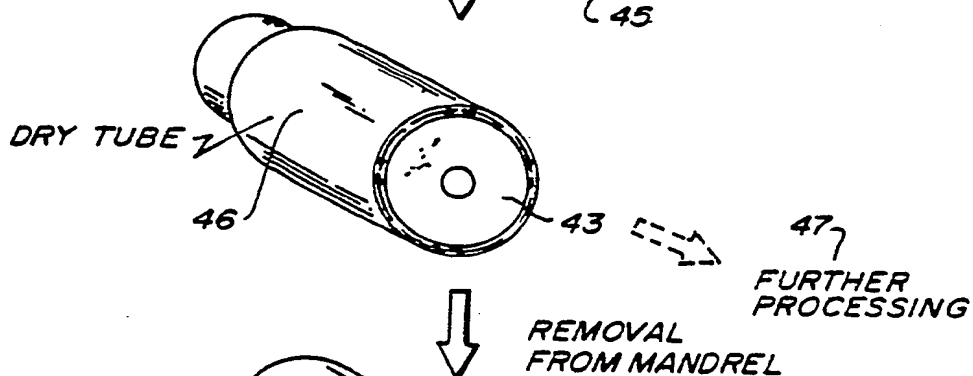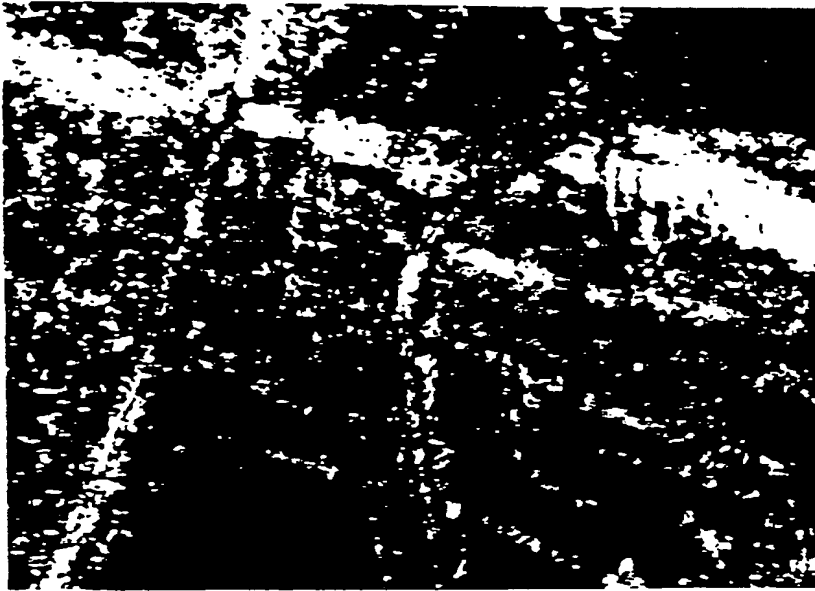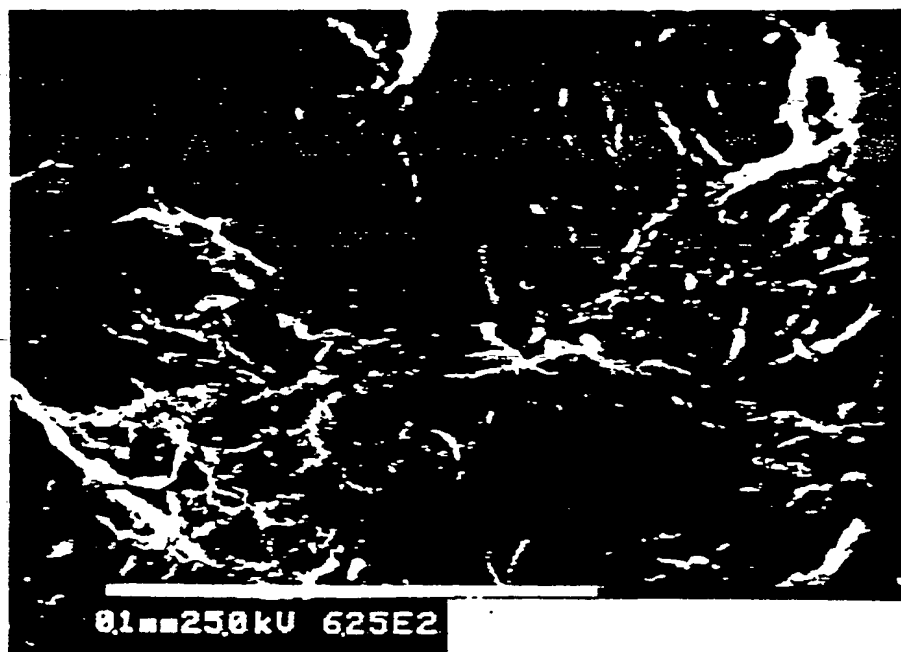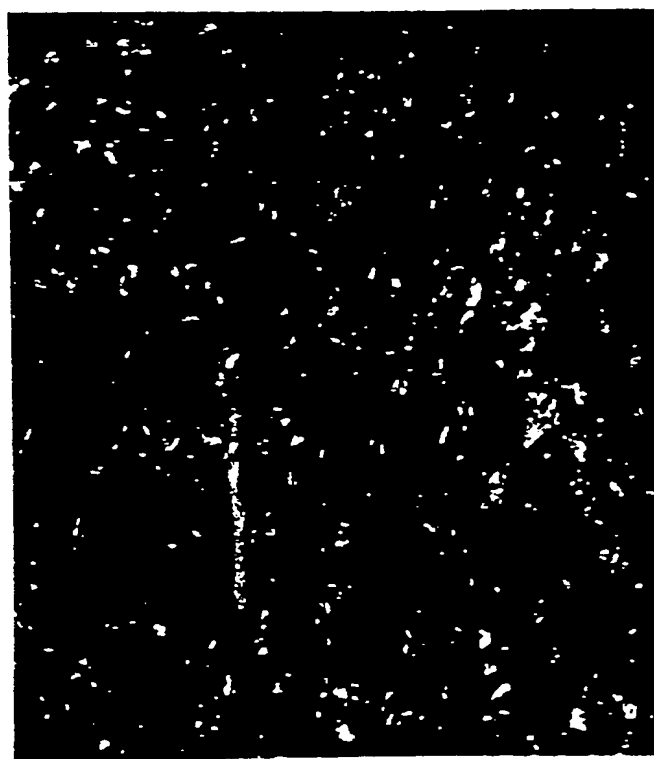
FIG. 4



FIG. 7

FIG. 5


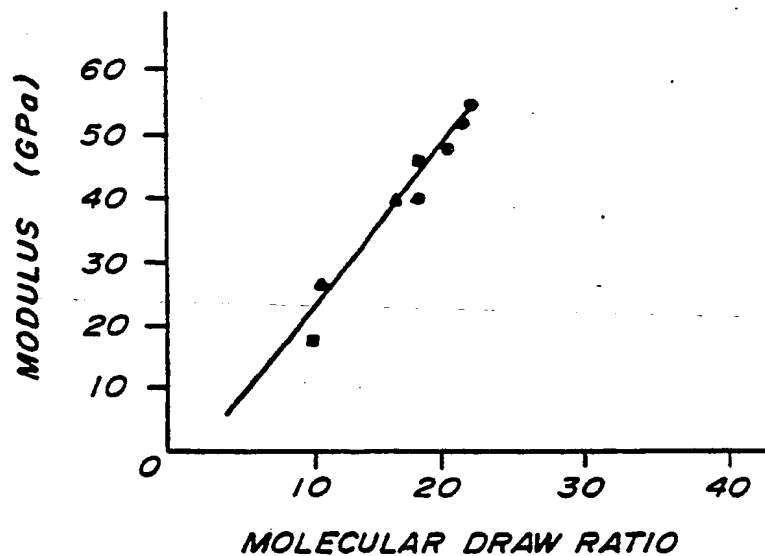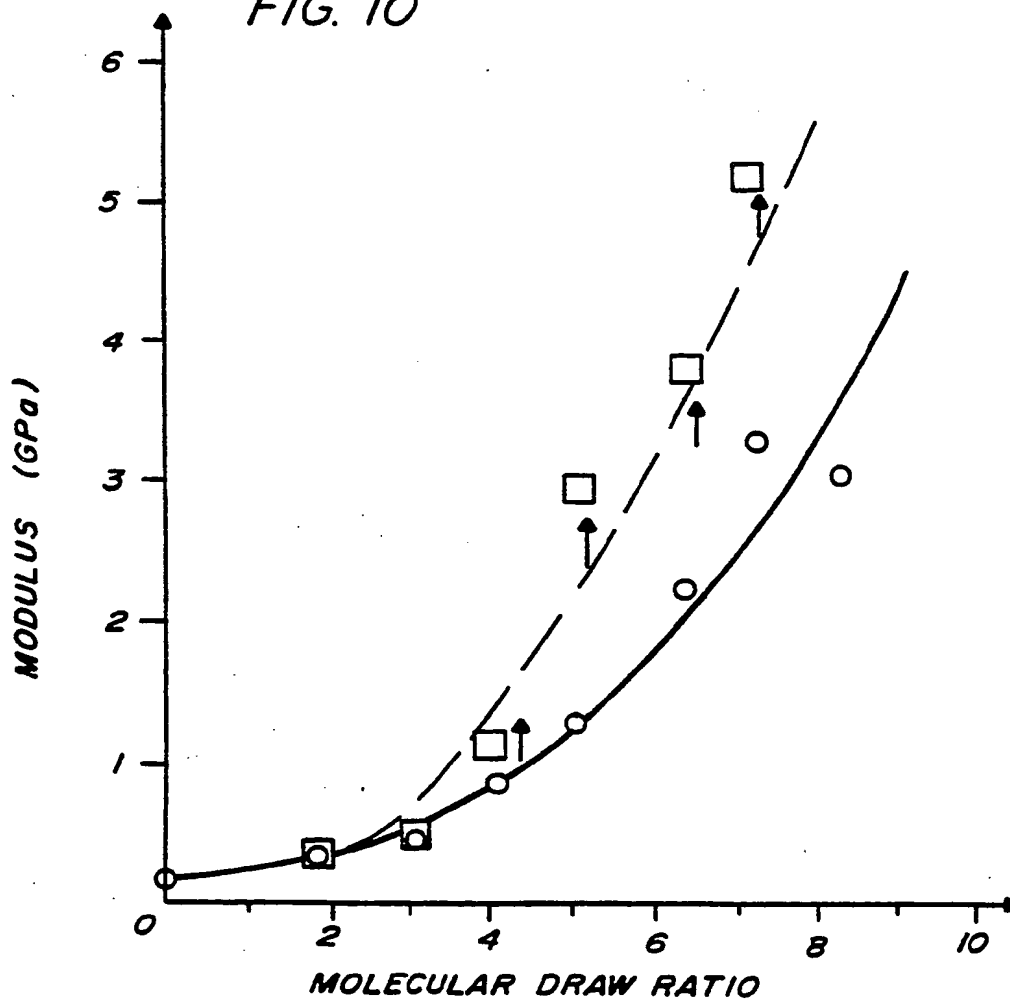
FIG. 6

FIG. 8



FIG. 9

*FIG. 11*



*FIG. 10*

# INTERNATIONAL SEARCH REPORT

International Application No  PCT/US85/02078

**I. CLASSIFICATION F SUBJECT MATTER** (if several classification symbols apply, indicate all) 3

Accc·ding to International Patent Classification (IPC) or to both National Classification and IPC

## IPC4 C08J 9/28

**II. FIELDS SEARCHED**

Minimum Documentation Searched 4

| Classification System | Classification Symbols |
|---|---|
| U.S. | 428/401 402; 526/352; 264/41, 49; 521/79, 143 524/585 |

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched 5



**III. DOCUMENTS CONSIDERED TO BE RELEVANT** 14

| Category * | Citation of Document, 16 with indication, where appropriate, of the relevant passages 17 | Relevant to Claim No. 18 |
|---|---|---|
| A | US, A, 3,954,927 PUBLISHED 04 MAY 1976 DULING ET AL | 1-37 |
| A | US, A, 3,984,387 PUBLISHED 05 OCTOBER 1976 LIU ET AL | 1-37 |
| A | US, A, 3,997,648 PUBLISHED 14 DECEMBER 1976 DAVIS ET AL | 1-37 |
| A | US, A, 4,020,266 PUBLISHED 26 APRIL 1977 FRANK ET AL | 1-37 · |
| A | US, A, 4,246,390 PUBLISHED 20 JANUARY 1981 SEAVER | 1-37 |
| A | US, A, 4,413,110 PUBLISHED 01 NOVEMBER 1983 KAVESH ET AL | 1-37 |

* Special categories of cited documents: 15
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"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

**IV. CERTIFICATI N**

| Date of the Actual Completion of the International Search 2 | Date of Mailing of this International Search Report 2 |
|---|---|
| 06 JANUARY 1986 | 2 4 JAN 1986 |
| International Searching Authority 1 | Signature of Authorized Officer 20 |
| ISA/US | P.R. Michl  *[signature]* |

Form PCT/ISA/210 (second sheet) (October 1981)